Understanding and characterizing the effect of nanoscale confinement on glass transition temperature and film dewetting of macrocyclic polystyrene

LANHE ZHANG, Materials Science and Engineering, Northwestern University, RAVINDER ELUPULA, SCOTT GRAYSON, Department of Chemistry, Tulane University, JOHN TORKELSON, Materials Science and Engineering, Department of Chemical and Biological Engineering, Northwestern University — There is a growing interest in the dynamics of different polymer topologies when confined to nanoscopic length scales. Macrocyclic polymers have attracted research interest because their lack of chain ends and cyclic topology has led to a range of unique physical properties. Cyclic polystyrene (c-PS) of well-defined molecular weight (MW) ranging from 2,300 to 8,700 g/mol was synthesized via click cyclization of dilute solutions of linear PS (l-PS) with azide and alkyne end functionalities. The click reaction enables nearly quantitative cyclization of l-PS. Differential scanning calorimetry was used to measure bulk glass transition temperature ($T_g$) and fragility of c-PS, both of which exhibit less MW dependence compared to l-PS. Compared to thin l-PS films, thin c-PS films exhibited extraordinary stability against dewetting. 22-nm-thick c-PS films were nearly stable for up to 4 hr at bulk $T_g + 45$ C; in contrast, 22-nm-thick l-PS films underwent severe dewetting. Nanoconfinement effects on $T_g$ and fragility of c-PS are investigated using ellipsometry and/or fluorescence spectroscopy and compared to effects for l-PS precursors as well as commercial anionic l-PS standards.

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